FLUORIDE / AZIDE LIGAND EXCHANGE REACTIONS

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Project Sponsors

Objective and Background

- Preparation and Characterization of High Energy Density Matter (HEDM) derived from binary covalent polyazides
- HN_3 was discovered in 1890 by Curtius, and binary covalent polyazides have been known for at least half a century ($B(N_3)_3$: Wiberg, 1954)
- Most compounds are extremely shock sensitive, difficult to handle and purify, and often have not been structurally characterized
- Important contributions to the field were made by Wiberg, Dehnicke, Schmidt, Roesky, Ang, Fillippou, and paricularly Klapoetke

Synthesis of Covalent Binary Polyazides

- Conventional methods involve the reactions of chlorides or iodides with either HN_3, NaN_3, AgN_3, or $(CH_3)_3SiN_3$

$$SbI_3 + 3\ AgN_3 \longrightarrow Sb(N_3)_3 + 3\ AgI$$

$$BCl_3 + 3\ HN_3 \longrightarrow B(N_3)_3 + 3\ HCl$$

$$PCl_5 + 6\ NaN_3 \longrightarrow NaP(N_3)_6 + 5\ NaCl$$

$$L{\cdot}BCl_3 + 3\ (CH_3)_3SiN_3 \longrightarrow L{\cdot}B\ (N_3)_3 + 3\ (CH_3)_3SiCl$$

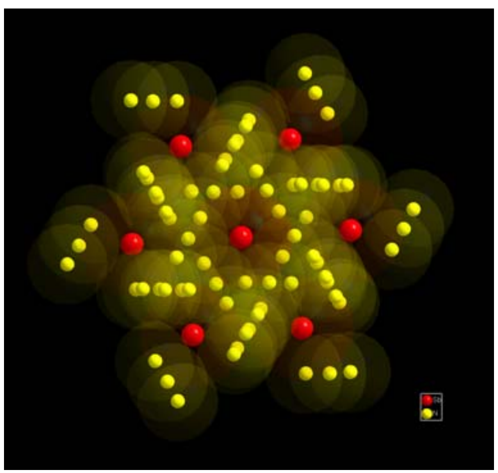
- Potential Problems with these methods
  - Shock sensitivity of AgN_3 and HN_3
  - Cl / N_3 ligand exchange is often incomplete
  - Solvent problems ($CH_2Cl_2 + 2\ MN_3 \longrightarrow CH_2(N_3)_2$)

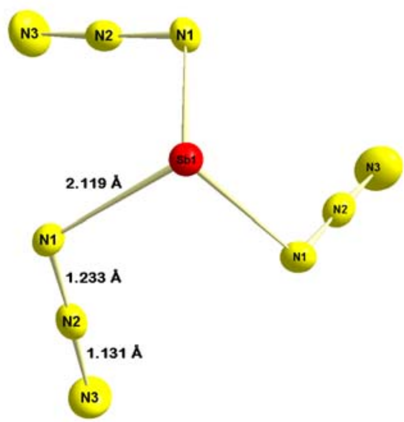
Our Method

- Use of fluorides with $(CH_3)_3SiN_3$ in a suitable solvent, such as SO_2 (-64 C), CH_3CN (-40 C), or excess $(CH_3)_3SiN_3$ (-40 C)
- Advantages
  - Rapid exchange
  - Complete conversions in a single step
  - Highly pure products
  - Easy product separation

Results from our Studies, $As(N_3)_3$ and $Sb(N_3)_3$

- $As(N_3)_3$ and $Sb(N_3)_3$ were previously known as highly explosive oil or powder, respectively, but no structures were known
- We obtained both compounds in crystalline form and determined their crystal structures






CHEMISTRY

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ISLE OF MAN

Concepts

Stabilization of p-Block Organoelement Terminal Hydroxides, Thiols, and Selenols Requires Newer Synthetic Strategies
H. W. Roesky et al.

High Oxidation-State Organometallic Chemistry in Aqueous Media: New Opportunities for Catalysis and Electrocatalysis
R. Poli

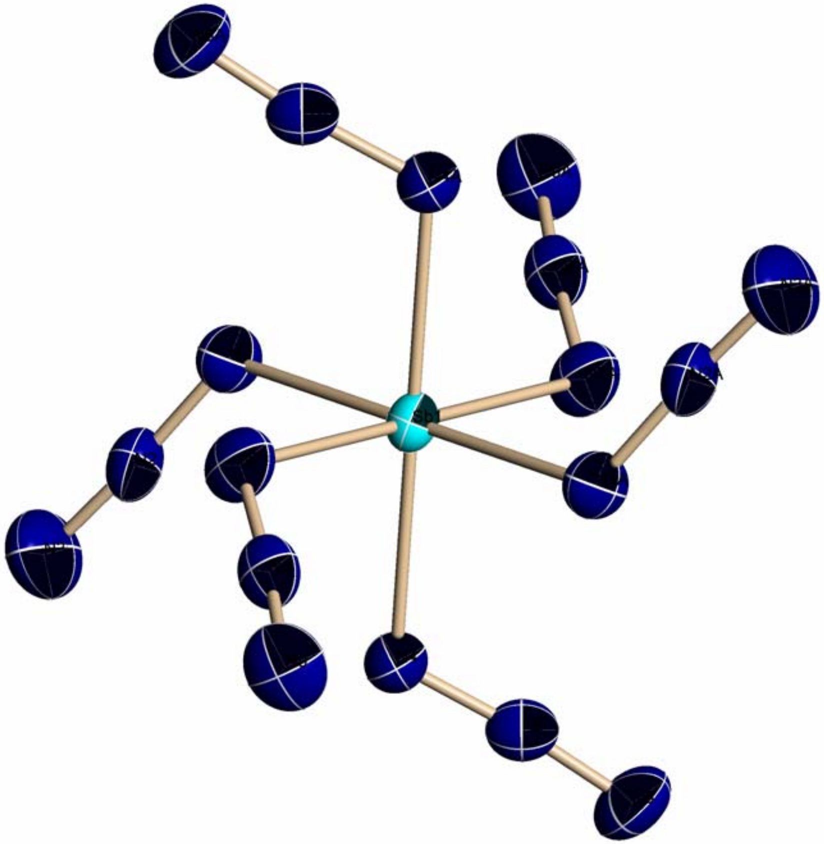
WILEY-VCH

EUChemSoc

CEUJED 10 (2) 313–560 (2004) · ISSN 0947-6539 · Vol. 10 · No. 2 · January 23, 2004

Crystal Structure of $[Sb(N_3)_6]^-$

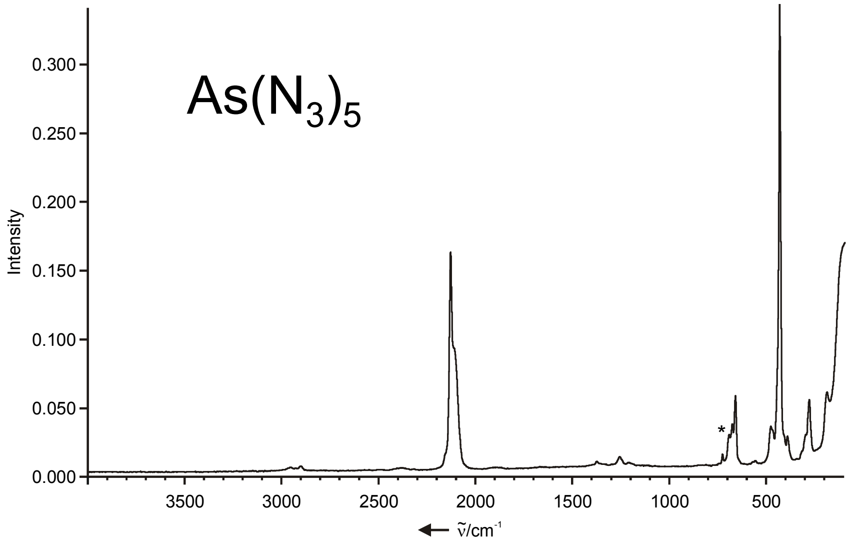
- $Sb(N_3)_6^-$ anion had been known, but its structure was unknown
- We prepared the $[P(C_6H_5)_4][Sb(N_3)_6]$ salt and determined its structure

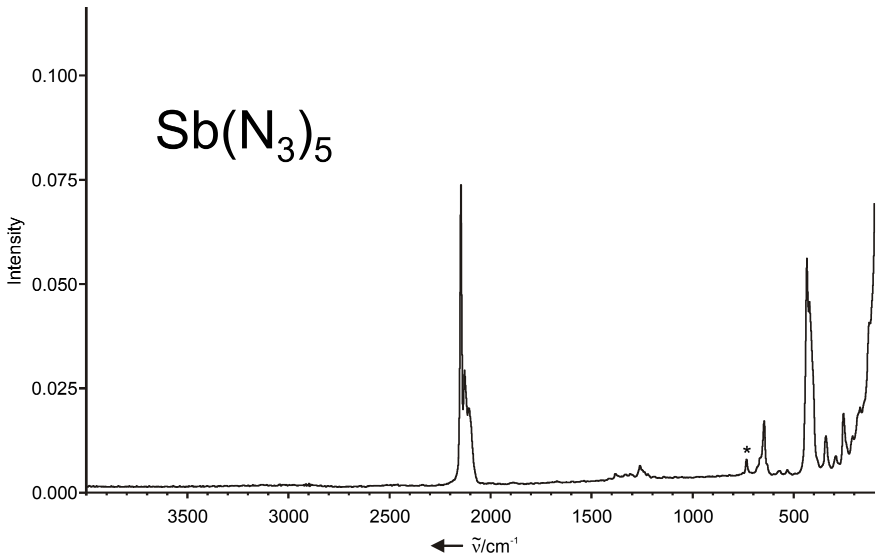


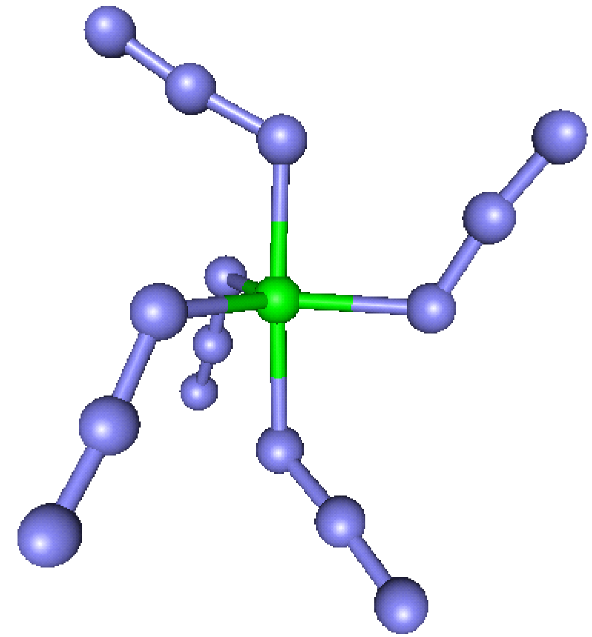
Syntheses and Vibrational Spectra of $As(N_3)_5$ and $Sb(N_3)_5$

- Neutral polyazides are generally the most sensitive and, therefore, most difficult to prepare and characterize
- Unstable neutral polyazides can usually be stabilized by
  - negative charges (anion formation)
  - adduct formation with large organic bases
  - large bulky inert spacers, such as cations, to stop propagation
- Although $M(N_3)_6^-$ anions and $M(N_3)_5$ donor-acceptor adducts with amines (M = As or Sb) had been known, the free pentaazides had been considered to be too sensitive for isolation
- The free pentaazides were now successfully prepared from the pentafluorides and TMSazide in SO_2 solution and characterized by low-temperature Raman spectroscopy and theoretical calculations

Raman Spectra of $As(N_3)_5$ and $Sb(N_3)_5$







- Good agreement between observed spectra and those calculated for trigonal-bypyramidal monomers

Tellurium Azides

• We prepared and characterized the novel $Te(N_3)_4$, $[N(CH_3)_4][Te(N_3)_5]$, and $[P(C_6H_5)_4]_2[Te(N_3)_6]$

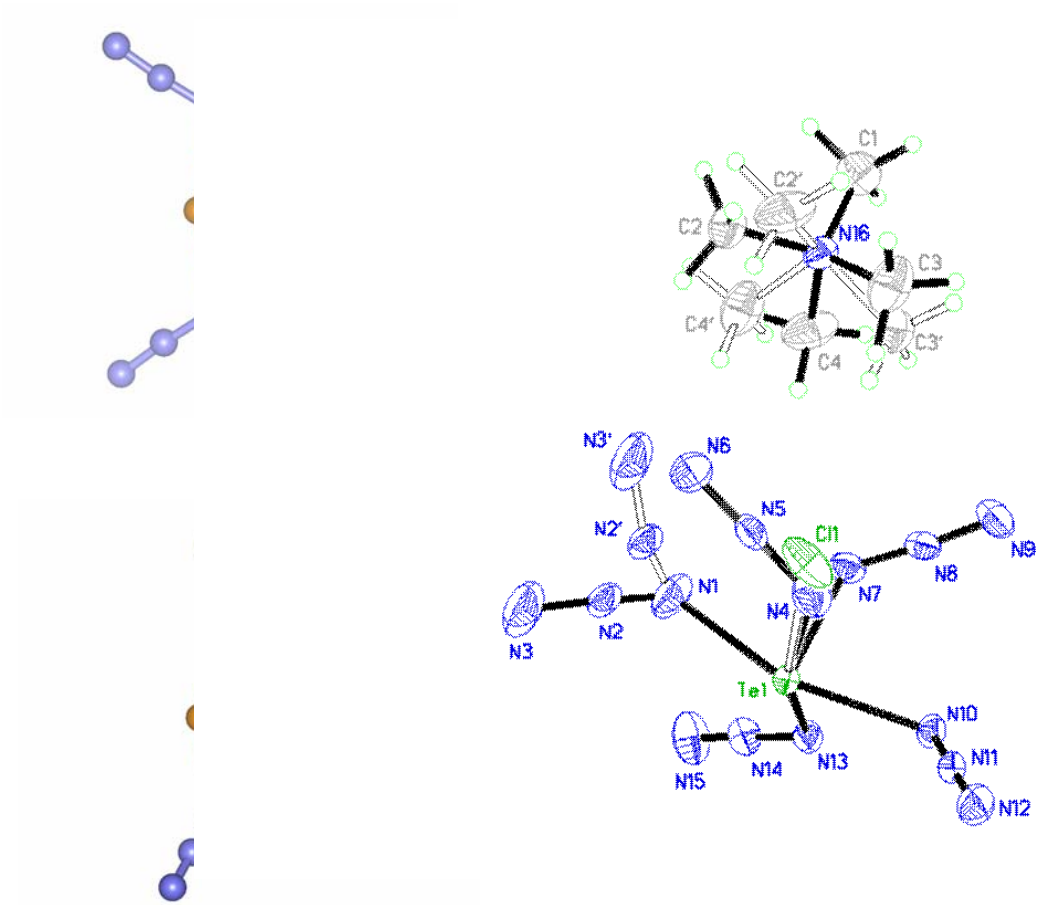
$$TeF_6 + 6\,(CH_3)_3SiN_3 \xrightarrow{CH_3CN,\ CsF\ cat} Te(N_3)_4 + 6\,(CH_3)_3SiF + 3\,N_2$$

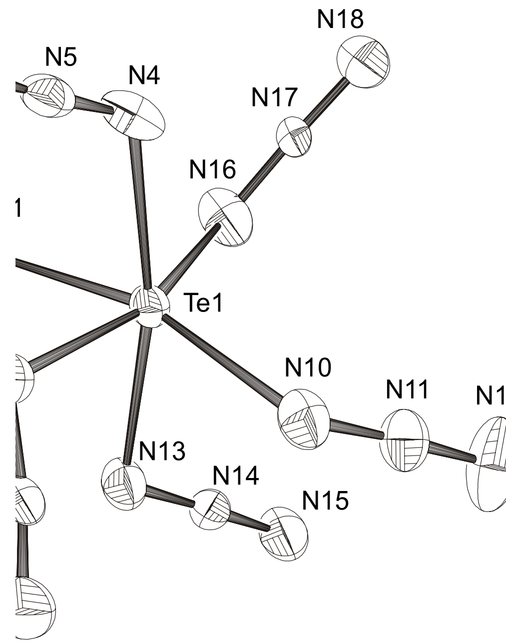
• $Te(N_3)_4$ is a shock sensitive, yellow solid and was characterized by vibrational and multinuclear NMRspectroscopy

•$Te(N_3)_5^-$ and $Te(N_3)_6^{2-}$ were characterized by their crystal structures

•The results were published in *Angew. Chem. Int. Ed.* **2003**, *115*, 1627 and highlighted in Chem. & Eng. News

Structures of $Te(N_3)_4$, $Te(N_3)_5^-$, and $[Te(N_3)_6]^{2-}$

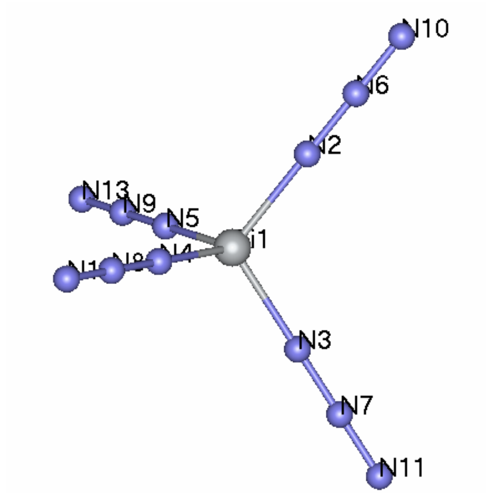


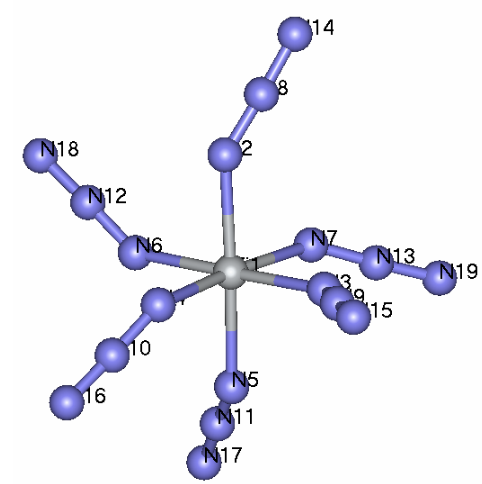


Titanium azide, does it possess linear Ti-N-N bonds?

- Based on quantum chemical calculations, Gagliardi and Pyykkoe have recently predicted, (*Inorg. Chem*. **2003**, *42*, 3074), for $Ti(N_3)_4$, $Zr(N_3)_4$, $Hf(N_3)_4$, and $Th(N_3)_4$ a novel type of bonding involving linear M-N-N bonds.

- We have confirmed these calculations for $Ti(N_3)_4$ and also predict that other azides, such as $Fe(N_3)_2$ (Melanie Teichert), can form linear M-N-N bonds. However, based on our calculations, we expect that the $Ti(N_3)_6^{2-}$ anion possesses the usual bent M-N-N bonds.





Synthesis and Characterization of $Ti(N_3)_4$

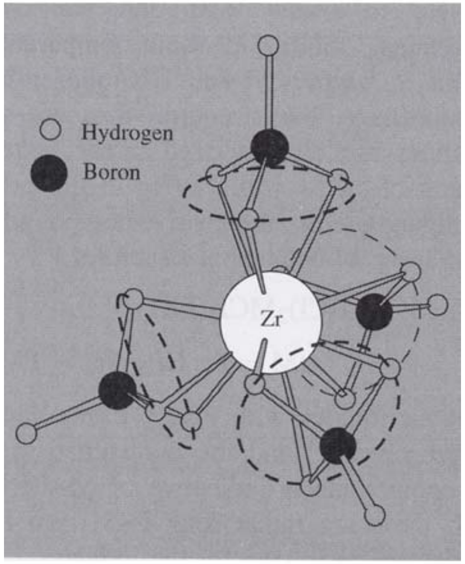
- Synthesis

$$TiF_4 + \text{exc. } TMSN_3 \rightarrow Ti(N_3)_4 + 4\ TMSF$$

- Properties
  - Yellow-orange solid
  - Very shock-sensitive
  - Very low volatility, decomposes on sublimation
  - Could not get single crystals for structure determination, but Raman spectrum and comparison with calculated spectra suggest that CN is higher than 4 and the Ti-N-N angle is bent.
  - Need a gas-phase structure of free $Ti(N_3)_4$

Possible explanations for linear M-N-N bonds

- Gagliardi and Pyykkoe invoke conjugation.
- We prefer the following interpretation because the calculated Ti-N bond distances are relatively long and are similar to single bonds. Also, the N_β-N_γ bonds are quite short, and the Ti-N-N bonds in $Ti(N_3)_6^{2-}$ are strongly bent.
  - The N_α atom of the $–N_3$ ligand has three free valence electron pairs which can act as a tridentate ligand and, in a tetrahedron, can perfectly overlap with three of the lobes of the Ti 3*d*-orbitals. This scheme is analogous to the structure of $Zr(BH_4)_4$ which possesses 4 trihapto BH_4 groups. In the usual covalent azides, the azide ligands utilize only one electron pair of the N_α atom for the bonding, and the presence of two additional, sterically active free valence electron pairs results in a pyramidal configuration with an M-N-N angle of about 120 °.

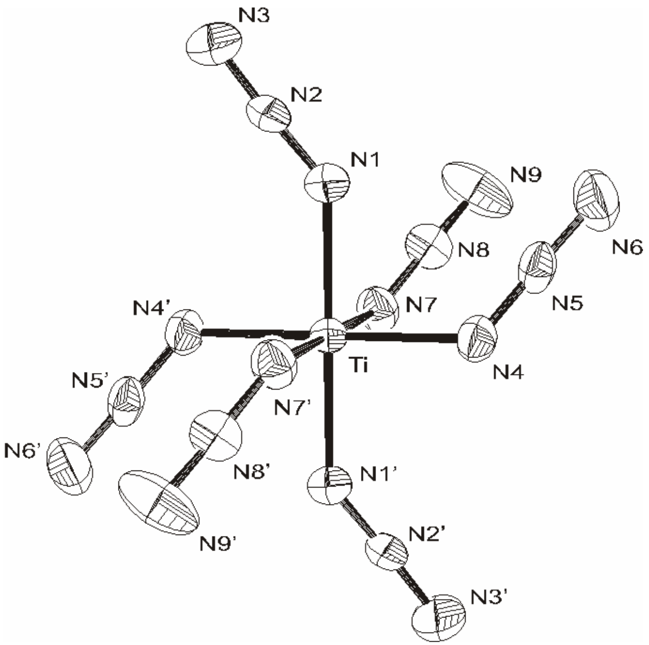


Crystal Structure of $[Ti(N_3)_6]^{2-}$

- Synthesized the $[Ti(N_3)_6]^{2-}$ anion according to

$$Ti(N_3)_4 \ + \ 2\ P(Ph)_4^+N_3^- \longrightarrow [P(Ph)_4]_2[Ti(N_3)_6]$$

and determined its crystal structure.



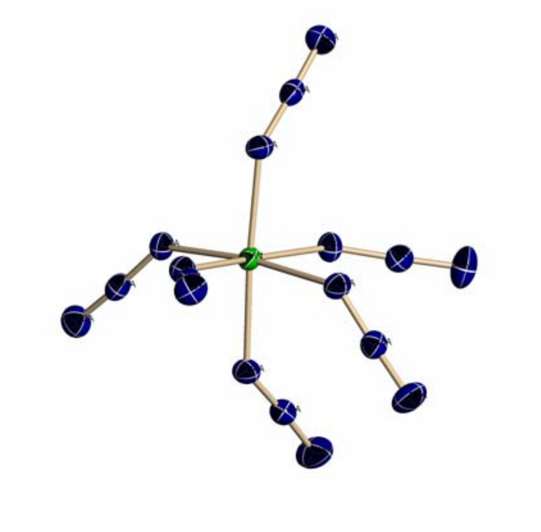
- Ti azide work has just appeared as a VIP paper in Angew. Chem. Int. Ed. **2004**, *116*, 3148.

Tantalum Azides

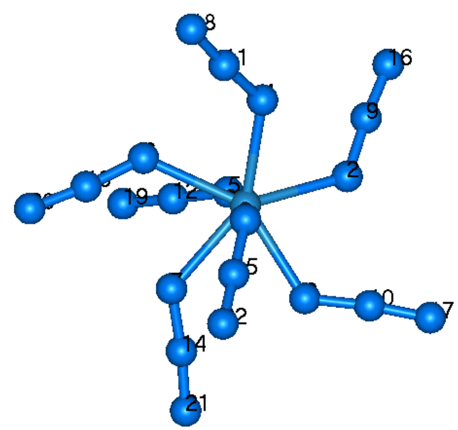
- $Ta(N_3)_5$ and $Ta(N_3)_6^-$, the first examples of binary Group V azides, were prepared from TaF_5 and were characterized by vibrational spectroscopy.
- $Ta(N_3)_5$ is very sensitive and unstable, whereas the $P(C_6H_5)_4^+Ta(N_3)_6^-$ salt is a stable white solid.

Molybdenum and Tungsten Azides

- $Mo(N_3)_6$ and $W(N_3)_6$, the first examples of binary Group VI azides, were prepared from MoF_6 and WF_6, respectively.
- Both compounds are highly shock sensitive and were characterized by low-temperature Raman spectroscopy and, in the case of WF_6, also by its crystal structure.
- $W(N_3)_6$ can be stabilized as its $P(C_6H_5)_4^+W(N_3)_7^-$ salt which was also characterized by vibrational spectroscopy.



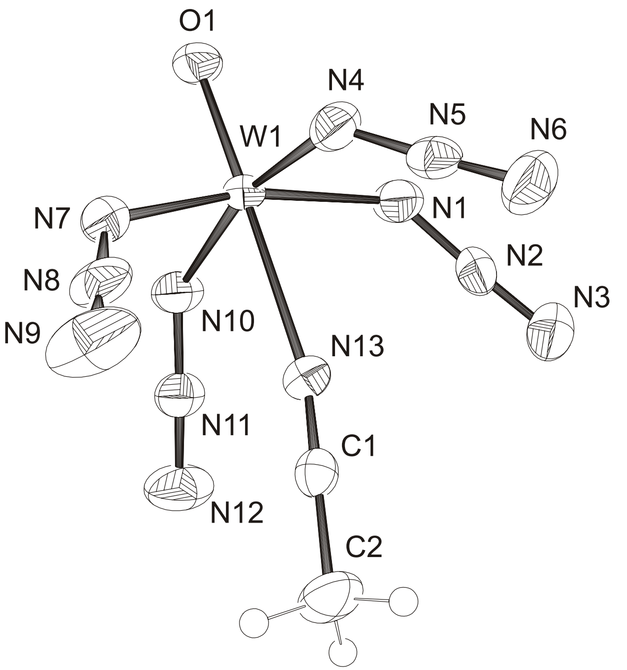
$W(N_3)_6$



$W(N_3)_7^-$

Oxoazides

- $WO(N_3)_4$, the first example of an oxoazide, was prepared from WOF_4 and characterized by vibrational spectroscopy
- Recrystallization from CH_3CN solution resulted in a hexa-coordinated structure
- The $P(C_6H_5)_4{}^+WO(N_3)_5{}^-$ salt was also prepared and characterized by vibrational spectroscopy



Combination of N_5^+ with $P(N_3)_6^-$ and $B(N_3)_4^-$

- First successful combinations of N_5^+ with highly energetic anions:

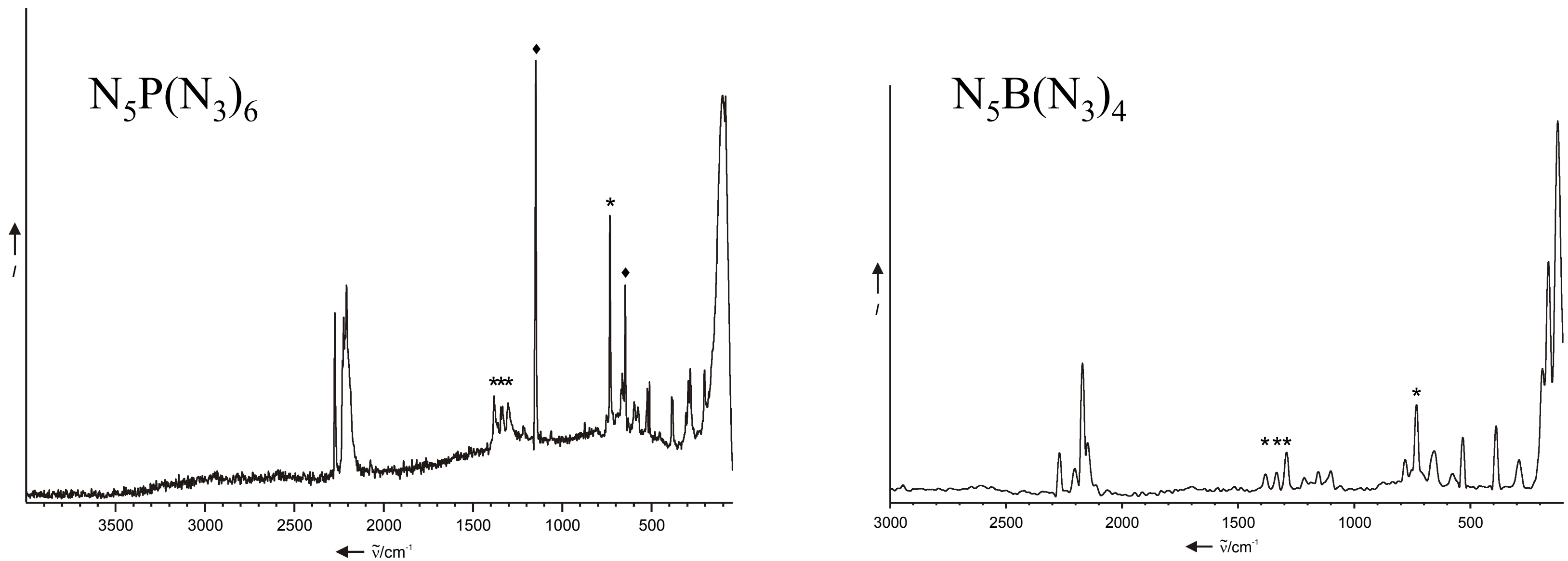
$$N_5SbF_6 + NaP(N_3)_6 \xrightarrow{SO_2,\ -64\ C} N_5P(N_3)_6 + NaSbF_6\downarrow$$

$$N_5SbF_6 + NaB(N_3)_4 \xrightarrow{SO_2,\ -64\ C} N_5B(N_3)_4 + NaSbF_6\downarrow$$

- $NaP(N_3)_6$ and $NaB(N_3)_4$ are already extremely shock-sensitive and their N_5^+ salts are even more vicious.
- $N_5B(N_3)_4$ contains 96 weight % of energetic nitrogen.
- Paper has been accepted by Angewandte for publication.

Characterization of $N_5P(N_3)_6$ and $N_5B(N_3)_4$

- Low-temperature Raman spectra



- Material balances
- Stable at -64 °C, explode on warm-up toward room temperature

Summary

- Fluorine compounds and trimethylsilylazide undergo rapid and quantitative fluoride / azide ligand exchange
- This reaction is ideally suited for the preparation of binary polyazides in high purity and quantitative yield
- Compounds studied so far under this program include:

  $W(N_3)_6$, $Mo(N_3)_6$, $W(N_3)_7^-$, $WO(N_3)_4$, $WO(N_3)_4 \cdot CH_3CN$, $WO(N_3)_5^-$, $Ta(N_3)_5$, $Ti(N_3)_4$, $Ti(N_3)_5^-$, $Ti(N_3)_6^{2-}$, $Te(N_3)_4$, $Te(N_3)_5^-$, $Te(N_3)_6^{2-}$, $Sb(N_3)_5$, $As(N_3)_5$, $Sb(N_3)_6^-$, $As(N_3)_3$, $Sb(N_3)_3$, $N_5^+B(N_3)_4^-$, and $N_5^+P(N_3)_6^-$

- This work is extremely challenging, because of the high energy content and explosiveness of these materials